

# THERMODYNAMIC THEORY OF ISOTOPE EFFECTS IN THERMODIFFUSION IN SILICATE MELTS

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Isotope effects in the thermodiffusion (IET) of liquids are examined using a non-equilibrium thermodynamic model, where the thermodynamic parameters are calculated using statistical mechanics. In this approach, isotope effects in thermodiffusion are quantified through the variation in chemical potential and its temperature dependence with isotope mass. The model is applied to silicate melts.

The model provides an adequate description of isotope effects in thermodiffusion in silicate melts, with reasonable theoretical values of the Soret coefficient. The Soret coefficients are calculated from the experimental isotope separation factors using the expressions derived in the work and compared with the literature data

## INTRODUCTION:

## PRESSURE OR CHEMICAL POTENTIAL?

The atomic mass is contained in terms of the partition function related to kinetic energy [1, 2]. Refs [1-3] demonstrate the utility of classical statistical mechanics in accounting for IET, without the need to invoke quantum contributions. In [4], quantum effects related to the mass difference were used to explain IET. The authors communicated an acceptable agreement with experimental data, but only by ignoring much larger classical contributions. This oversight is due to expressing thermodiffusion parameters through the pressure [5, 6], which is proportional to the volume derivative of the partition function:

Pressure

$$P = -kT \frac{\partial}{\partial V} \ln Z$$

Partition function

Volume of system

However according to [2, 3] the mass dependent terms are not dependent on the volume. According to Refs [2], [7], the partition function mentioned in Ref. [4] can be written as

Classic partition function

Planck constant and frequency of librations

$$Z = Z_{classic} \left[ 1 - \frac{1}{24} \left( \frac{h\omega}{kT} \right)^2 \right]$$

Quantum contribution used in [4] which is  $\approx 10^{-3} Z_{classic}$

The classical mass-dependent terms in the partition function are related to kinetic energy, not volume. The much larger classical terms in the material transport parameters corresponding to kinetic energy of the translational and rotational motion are lost if the pressure is used as the main thermodiffusion parameter.

The theory of material transport in non-equilibrium thermodynamics should use chemical potentials

$$\mu_i = -kT \frac{\partial}{\partial N_i} \ln Z_i$$

Number of i-th isotope atoms

as the relevant parameters.

# MATERIAL TRANSPORT EQUATIONS

For calculations we use the material transport equations derived in [8], which are the standard equations of non-equilibrium thermodynamics with certain restrictions placed on the Onsager kinetic coefficients, in order to provide the unique solution. The general mass transport equation based on non-equilibrium thermodynamics for component  $i$  in an  $N$ -component mixture is:

Stokes-Einstein  
diffusion  
coefficient

Binary chemical potential  $\mu_{ik}^* = \mu_i - \frac{v_i}{v_k} \mu_k$  expressed  
through the chemical potentials  $\mu_i$  of components

Volume  
fraction

Time

$$\frac{\partial \phi_i}{\partial t} = \nabla \phi_i \frac{D_i}{2kT} \frac{\sum_{j=1}^N \phi_j v_j D_j \left( 2 \sum_{k>1}^N \frac{\partial \mu_{ij}^*}{\partial \phi_k} \nabla \phi_k + \frac{\partial \mu_{ij}^*}{\partial T} \nabla T \right)}{\sum_{k=1}^N \phi_k v_k D_k}$$

Partial molecular volume

## Studies of IET involve measurements of the isotope separation parameter:

Volume fraction

$$\delta_{ij} = \frac{\phi_i(l)/\phi_i(0)}{\phi_j(l)/\phi_j(0)} - 1 \quad (1)$$

at points  $0$  and  $l$  along the temperature gradient. The parameter  $\delta_{ij}$  can be expressed through the Soret coefficients  $S_T$  of the respective components [9-14]:

$$\delta_{ij} = -(S_T^i - S_T^j)[T(l) - T(0)] \quad (2)$$

For dilute isotopes,  $\mu_{ik}^*(\phi_i) \approx kT \ln \phi_i$  [7], and the isotope separation parameter is:

$$\delta_{ij} = -\frac{\partial}{\partial T} \left( \frac{\mu_{i1}^* - \mu_{j1}^*}{2k} \right) \frac{T(l) - T(0)}{T(0)} \quad (3)$$

where subscript  $1$  refers to the solvent component in a dilute mixture of isotopes.

# STATISTICAL-MECHANICAL CALCULATION OF CHEMICAL POTENTIAL AT CONSTANT VOLUME

According to [15, 16], the chemical potential is defined by the expression

$$\mu_i = \mu_{0i} + 4\pi \int_0^1 d\lambda \int_R^\infty \frac{g_{i1}(r, \lambda)}{v_1} \Phi_{i1}(r) r^2 dr \quad (4)$$

Here,  $R$  is the particle radius and  $r$  is the distance between a solvent molecule and the solute,  $g_{i1}(r, \lambda)$  is the pair correlation function, and  $\Phi_{i1}(r)$  is the interaction potential.

$m_i$  is the atomic or molecular mass

$$\mu_{0i} = kT \ln \phi_i v_i - \frac{3}{2} kT \ln \left[ \frac{2\pi m_i kT}{h^2} \right] \quad (5)$$

is the chemical potential of the non-interacting solute. Parameter  $\lambda$  describes the gradual “switching on” of the intermolecular interaction [15, 16].

We will use the approximation:

$$g_{21}(r, \lambda) = 1 \quad (6)$$

This approximation means that the local distribution of solvent molecules is not disturbed by the particle under consideration (regular solution).

The approximation of constant local density leads to the following equation:

$$\mu_i = \mu_{0i} + 4\pi \int_R^{\infty} \frac{\Phi_{i1}(r)}{v_1} r^2 dr \quad (7)$$

The last term on the right-hand side was obtained earlier in Refs. [17-19].

The expression for the binary chemical potential at constant volume  $\mu_{i1}^*$  is

$$\mu_{i1}^* = -\frac{3}{2} kT \ln \left( \frac{m_i}{m_{i1}} \right) + 4\pi \int_R^{\infty} \frac{\Phi_{i1}(r) - \Phi_{11}(r)}{v_1} r^2 dr \quad (8)$$

Mass of the solvent material displaced  
from the volume occupied by i-th solute

The chemical potentials at constant pressure and volume can be related by expressing the forces acting on the particle:

$\Pi_i$  is the local distribution of the excess pressure around the solute

$$\nabla \mu_p^i = \nabla \mu_i + \int_{V_{out}^i} \nabla \Pi_i dv \quad (9)$$

In deriving the local excess pressure we follow the method outlined in Ref. [20] using the condition of equilibrium in a spherical layer around the considered particle. The excess pressure contains two terms related to the change of the radial position of the spherical layer and its surface area.

$$\Pi_i = -\frac{\Phi_{i1}(r)}{v_1} - \int_{\infty}^r \frac{2\Phi_{i1}(r')}{v_1 r'} dr' \quad (10)$$

Using Eqs (8-10) and calculating the pressure gradient related we obtain the temperature derivative of the chemical potential:

Coefficient of  
thermal  
expansion

$\Phi_{i1} = -\varepsilon_{i1} \left( \frac{\sigma_{i1}}{r} \right)^6$  is London potential,

where  $\varepsilon_{i1}$  is energetic parameter and  $\sigma_{i1}$  is the minimal atomic approach distance

$$\frac{\partial \mu_P^i}{\partial T} = \frac{2\alpha_T}{v_1 |\nabla T|} \int_{V_{out}^i} dv \nabla_g T \int_{\infty}^r \frac{\Phi_{i1}(r')}{r'} dr' - \frac{3k}{2} \ln \left( \frac{m_i}{m_{i1}} \right) \quad (11)$$

Temperature gradient tangent  
to surface of spherical particle



The molecular Soret coefficient can be written as

$\frac{m_i}{m_{i1}}$  may be approximated as the ratio of solute-to-solvent densities  $\frac{\rho_i}{\rho_1}$

$$S_T^i = S_T^{0i} - \frac{3}{4T} \ln \left( \frac{m_i}{m_{i1}} \right) \quad (12)$$

$S_T^{0i} = \frac{\pi^2 \alpha_T \sigma_{i1}^3 (\epsilon_{11} - \epsilon_{i1})}{9v_1 kT}$  is the term related to intermolecular interactions

The difference in Soret coefficients for isotopes is:

$$\begin{aligned} S_T^i - S_T^j &= \\ &= \frac{m_i - m_j}{m_i} \left[ \frac{\partial \ln \sigma_{j1}^3}{\partial m} - \frac{\partial \ln (\epsilon_{11} - \epsilon_{j1})}{\partial m} \right] S_T^{0j} - \\ &\quad - \frac{m_i - m_j}{m_i} \left( 1 - \frac{\partial \ln \sigma_{j1}^3}{\partial m} \right) \frac{3}{4T} \end{aligned} \quad (13)$$

# MOLECULAR VOLUMES AND ENERGETIC PARAMETERS OF ISOTOPES ARE DIFFERENT

This fact is demonstrated by the separation of isotopes in liquids by diffusion [21]. The diffusion coefficients have been shown to fit the equation:

$\beta$  is the empiric dimensionless parameter

$$\frac{D_i}{D_j} = \left( \frac{m_j}{m_i} \right)^\beta \quad (14)$$

Then we can write

$$\frac{\sigma_{i1}}{\sigma_{j1}} = \left( \frac{M_i}{M_j} \right)^\beta \quad (15)$$

There are also the data regarding the mass dependence of the energetic parameters [22]. For this reason we assume that the mass dependence of the isotope energetic parameters is also described in the similar way

Eq. (13) can be written as

$$S_T^i - S_T^j = \frac{m_i - m_j}{m_i} \left[ \beta \left( 4S_T^{0j} + \frac{9}{4T} \right) - \frac{3}{4T} \right]$$

(16)

## COMPARISON WITH EMPIRICAL DATA

Eq. (16) can be used to compare the model with empirical data expressing  $\delta_{ij}$  in as

$\alpha_0$  is an empirical parameter characterizing IET

$$\delta_{ij} = -\alpha_0 \frac{m_i - m_j}{m_i + m_j} \frac{T(l) - T(0)}{T(0)} \quad (17)$$

Combining Eqs (2), (16), and (17), we obtain the theoretical expression for  $\alpha_0$

$$\alpha_0 = \beta \left[ 8 \left( TS_T^j + \frac{3}{4} \ln \frac{\rho_j}{\rho_0} \right) + \frac{9}{2} \right] - \frac{3}{4} \quad (18)$$

Eq. (18) is used to calculate the theoretical values of the Sore coefficients for different atomic species in the basalt melt and compare them with the empirical data. The results are present in Table I.

**TABLE I. MAIN RESULTS\***

Isotope Pair	Index of power $\beta$ for mass dependence of atomic size and energetic parameter [23]	Isotope separation factor $\alpha_0$ [11]	Calculated Soret coefficient ( $10^3 \text{ K}^{-1}$ )	Experimental Soret coefficient ( $10^3 \text{ K}^{-1}$ ) [23]	Density of isotopes, $\text{g/cm}^3$
$^{56}\text{Fe}/^{54}\text{Fe}$	0.03	0.137	2.5 - 2.6	1.9 – 2.5	6.98
$^{44}\text{Ca}/^{40}\text{Ca}$	0.075	0.239	1.1 – 1.2**	0.5 – 0.7	1.55
$^{26}\text{Mg}/^{24}\text{Mg}$	0.05	0.376	1.9 - 2.0**	1.6 – 1.9	1.75

\*The density of basalt is assumed to be  $3.0 \text{ g/cm}^3$ .

\*\*Calculated taking not into account mass dependence of energetic parameter

**In conclusion, the present theory yields an adequate description of IET in silicate melts, providing reasonable values of the Soret coefficients given the coarse approximations utilized. The model relates IET to differences in the thermal velocities of isotopes having the same thermal energy but different masses, which is not possible using methods described previously.**

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